CVD of PtRh WITH GOOD ADHESION AND MORPHOLOGY

Background of the Invention

Field of the Invention

The present invention relates to semiconductor processing and, in particular, concerns a chemical vapor deposition (CVD) technique for forming conductive layers, such as platinum-rhodium layers, in a manner that results in better adhesion of the component layer on the surface of a semiconductor device and better morphology of the layer.

Description of the Related Art

Modern semiconductor chemical vapor deposition (CVD) technology has provided fabrication procedures for the development of VLSI (Very-Large-Scale Integration) and ULSI (Ultra-Large-Scale Integration) circuitry. Even though the number of surface mounted semiconductor devices has significantly increased, the surface density is often limited by the finite quantity of real estate on the semiconductor wafer surface. As a result, the finite surface density limitation has induced growth in the vertical direction of modern semiconductor devices. This often requires multiple levels of the conductive interconnects that often, in turn, require numerous metallic-based deposition layers.

As the size of the conductive elements has decreased to accommodate higher density of components, many conventional semiconductor processing techniques for forming conductive elements are forming conductive elements that exhibit more gaps and pinholes and poorer adhesion to the substrate. One particular CVD deposition technique utilized for forming conductive elements is Metal-organic Chemical Vapor Deposition (MOCVD). However, conventional MOCVD techniques alone cannot

always compensate for the relatively poor adhesion and morphology that occurs in smaller devices.

For example, complex chemical reactions that occur during the formation of semiconductor devices dictate the final composition of the deposited layer, which may be different than the intended composition. Specifically, the grain structure within the deposited layer may vary depending on the growth rate and the growth environment during the manufacturing and deposition process. A variance in the grain size and grain structure within deposited layers of similar composition and thickness may interfere with or alter the conduction characteristics of electrical current flow through the grain interfaces.

A typical MOCVD technique is as follows. A precursor gas, comprising at least one conductive component or element, and other reactants are introduced into a CVD chamber, and the conductive element carried by the precursor gas is then deposited onto the semiconductor surface of the semiconductor substrate through thermal decomposition. The precursor gas may often be a metal-organic compound, wherein conductive atoms may be bonded to organic compounds, which allows the conductive atoms to be transferred to the semiconductor surface in a gas phase. This enables the conductive atoms, such as platinum and rhodium, to be deposited over the surface of the semiconductor substrate surface as the metal-organic compound facilitates conventional step coverage.

In the prior art, there is generally only a single deposition step such that the precursor gas is introduced into the CVD chamber until enough conductive molecules have been deposited on the exposed semiconductor surface to form a conductive element of a desired thickness. However, as discussed above, conventional MOCVD techniques can result in poor adhesion and poor morphology of the deposited conductive element. This problem is exacerbated in higher density applications requiring smaller conductive components.

From the foregoing, it will be appreciated that there is a need for an improved conductive layer processing technique for depositing, in one embodiment, conductive materials onto a semiconductor substrate surface such that improved substrate adhesion and improved morphology may be obtained without a significant increase in the cost of manufacturing the conductive film layer. To this end, there is also a need for a more efficient method of depositing conductive elements, such as platinum and rhodium, in a manner that exhibits an improved grain interface structure and greater compositional uniformity.

Summary of the Invention

The aforementioned needs are satisfied by the present invention which, in one aspect is comprised of a method of forming a conductive layer on a substrate. In this aspect, the method comprises positioning the substrate in a chemical vapor deposition (CVD) chamber and then introducing at least one precursor gas, having at least one conductive component and at least one organic component, into the CVD chamber. A first reactant gas is then introduced into the chamber so as to disassociate the at least one conductive component from the at least one organic component at one activation energy so as to result in a first layer of conductive material being formed on the substrate. A second reactant gas is then introduced into the chamber after introducing the first reactant gas so as to disassociate the at least one conductive component from the at least one organic component at another activation energy greater than the first energy so as to result in columnar growths of conductive material from the first layer of the conductive material formed on the substrate. The method further comprises re-introducing the first reactant gas into the chamber so as to planarize the conductive film by filling in gaps between the columnar growths of the conductive material.

In one embodiment, the first reactant gas is a reducing gas and the second reactant gas is an oxidizing gas. The use of the reducing gas results in reduced surface mobility of the atoms which results in greater step coverage and promotes better

adhesion. The periodic use of the oxidizing gas results in greater surface mobility causing the atoms to agglomerate together which promotes faster columnar growths. The periodic reintroduction of the first reactant gas, however, results in better filling in of the gaps and pin holes resulting from the faster columnar growths. In one specific embodiment, the at least one precursor gas is a mixture of gases, which comprises platinum, rhodium, or a combination thereof. In another specific embodiment, a plurality of precursor gases may be used, wherein a first precursor gas comprises a platinum component and a second precursor gas comprises a rhodium component.

In another aspect of the invention, the invention comprises a method of forming a conductive structure on a semiconductor substrate. The method comprises (i) performing a first metal-organic chemical vapor deposition step using a first chemistry selected to provide more uniform coverage of the semiconductor substrate and (ii) performing a second metal-organic chemical vapor deposition step using a second chemistry selected to provide for increased columnar growth. The method further comprises alternating the acts (i) and (ii) until a conductive structure of a pre-selected thickness is formed on the semiconductor substrate so that the performance of the first metal-organic chemical vapor deposition act decreased gaps and pin holes formed during the performance of the second metal-organic chemical vapor deposition act.

In yet another aspect of the invention, the invention comprises a system for forming a conductive element on a semiconductor device. The system comprises a CVD chamber that receives the semiconductor device. The system also includes a precursor gas supply system that provides at least one precursor gas to the CVD chamber, wherein the at least one precursor gas comprises conductive components that when deposited on the semiconductor device form the conductive element and organic components which facilitate step coverage of the conductive element over the semiconductor device. The system also includes a reactant gas supply system that provides both a first reactant and a second reactant into the chamber so that the precursor gas is deposited using both a first chemistry and a second chemistry such that

the first chemistry provides more uniform step coverage and the second chemistry provides increased vertical growth of the conductive element, which is comprised by the at least one precursor gas, on the semiconductor substrate.

The aspects of the present invention result in a process or system for forming conductive elements that is both efficient and leads to improved morphology and adhesion. These and other objects and advantages will become more apparent from the following description taken in conjunction with the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a schematic illustration of a system block diagram, which depicts one embodiment of a deposition system for the formation of a conductive structure on a semiconductor device;

Figures 2A-2E are cross-sectional views of a semiconductor device illustrating one embodiment of a method, whereby a conductive structure is formed on the semiconductor device;

Figure 3A is a graphical illustration of a typical platinum precursor gas molecule used in a CVD process;

Figure 3B is a graphical illustration of a typical rhodium precursor gas molecule used in a CVD process;

Detailed Description of the Preferred Embodiment

Reference will now be made to the drawings wherein like numerals refer to like parts throughout. Figure 1 is a block diagram of one embodiment of a deposition system 100 for the formation of a conductive structure or element of the present invention. As is illustrated in Figure 1, a chemical vapor deposition (CVD) chamber 102, of a type known in the art, is supplied with precursor gases 104a, 104b that is utilized to deposit conductive layers and structures on semiconductor devices positioned within the CVD chamber 102. In particular, a carrier gas 106 from a carrier gas source

116 is supplied to a bubbler 114, which, in this embodiment, comprises a first metal-organic liquid precursor 108 and a second metal-organic liquid precursor 110.

Additionally, the carrier gas 106 is utilized to carry the vapor of the conductive metal-organic components comprised by the liquid precursors 108 and 110. Furthermore, a first metal-organic precursor gas 104a develops from the first metal-organic liquid precursor 108, and a second metal-organic precursor gas 104b develops from the second metal-organic liquid precursor 110. In one embodiment, the precursor gases 104a, 104b may be introduced separately, in either a simultaneous manner or at pre-determined temporal intervals, to the CVD chamber 102 in a manner known in the art. In another embodiment, the precursor gases 104a, 104b may be mixed within the bubbler chamber 122 so as to form a precursor gas mixture that may then be introduced to the CVD chamber 102 in a manner known in the art.

In one preferred embodiment, the carrier gas 106 is a known helium-based inert gas, which serves to carry the vapor of the liquid precursors 108 and 110. The inert helium-based carrier gas 106 is supplied to the bubbler 114, which houses the first metal-organic liquid precursor 108, such as, for example, methylcyclopentadienyl trimethyl platinum ($MeCpPtMe_3$) (See, Figure 3A), and the second metal-organic liquid precursor 110, such as, for example, Dicarbonyl Cyclopenda Dienyl Rhodium (DCDR)(See, Figure 3B). The carrier gas 106 carries the vapor of the liquid precursors 108 and 110, which may comprise the platinum-based metal-organic components and the rhodium-based metal-organic components. In one aspect, the platinum-based metal-organic vapor and the rhodium-based metal-organic vapor may then be mixed in the bubbler chamber 114 and subsequently introduced to the CVD chamber 102 for a pre-selected period of time so as to allow the conductive metal-organic components to coat the semiconductor device via chemical vapor deposition techniques. In another aspect, the first precursor gas 104a, such as the platinum-based metal-organic vapor, and the second precursor gas 104b, such as the rhodium-based metal-organic vapor, may be separately introduced to the CVD chamber 102 for a pre-selected period of time so as to

allow the conductive metal-organic components to coat the semiconductor device via chemical vapor deposition techniques.

While in this particular embodiment, the metal-organic precursor gases 104a, 104b have platinum-based and/or rhodium-based components, it will be appreciated that any of a number of different precursor gases and/or vapors may be used without departing from the scope of the present invention. These metal-organic gases and/or vapors include, but are not limited to, gases and/or vapors that entrain conductive elements such as Pt, Rh, Ir, Ni, Co, Cu, W, and the like or any combination thereof.

As is also illustrated in Figure 1, the deposition system 100 includes a first reactant source 122 that provides a first reactant vapor 126 and a second reactant source 124 that provides a second reactant vapor 128 into the CVD chamber 102 that are alternatively selected so as to interact with the conductive metal-organic compounds of the precursor gases 104a, 104b to thereby facilitate more a more uniform and efficient deposition of the conductive metal-organic molecules comprised by the precursor gases 104a, 104b. Providing the reactant vapors, 126 and 128, into the CVD chamber 102 allows the metal-organic molecules comprised by the precursor gases 104a, 104b to deposit on the surface of the semiconductor device that is positioned within the CVD chamber 102. As is also illustrated in Figure 1, the illustrated chemical vapor deposition system 100 also includes a waste gas receptacle 130 that receives waste gas 132, which may comprise unused precursor gases 104a, 104b, unused reactant vapors, 126, 128, and other reaction by-products produced during the CVD process. In the preferred CVD process, the first reactant vapor 126 is a reducing agent, such as diatomic hydrogen or a hydrogen derivative (H_2), and the second reactant vapor is an oxidizing agent, such as diatomic oxygen or an oxygen derivative (NO, N_2O, O_2, or O_3).

Figures 2A-2E are cross-sectional views of a semiconductor device 200 depicting one embodiment of a deposition process and method of the illustrated embodiment in greater detail, whereby a conductive structure is formed on the semiconductor device 200. As is illustrated in Figure 2A, a semiconductor device 200,

which may comprise a semiconductor substrate 202 with a surface 204, is positioned within the CVD chamber 102. The precursor gases 104a, 104b are introduced into the CVD chamber 102 such that a conductive material, such as platinum-rhodium (PtRh), is deposited on the exposed surface 204 of the semiconductor device 200. The deposition process begins with a nucleation process, wherein nucleation sites develop as the first few metal-organic molecules are deposited onto the semiconductor substrate surface 204. The nucleation process involves the first reactant vapor 126, which is simultaneously introduced into the CVD chamber 102 along with the precursor gases 104a, 104b. The first reactant vapor 126 is preferably selected to serve as a reducing agent that reacts with the precursor gases 104a, 104b. Additionally, the resulting reduction chemistry may offer a more uniform nucleation on the semiconductor substrate surface 204, which may possibly be due to its comparatively low reaction energy and comparatively resulting low surface mobility. In one particular embodiment, the first reactant vapor 126 includes a hydrogen based gas, such as a gas selected from the group of H_2, NH_3 or H_2O.

The comparatively low reaction energy may provide for a comparatively low surface mobility as the metal-organic molecules adhere more readily to the semiconductor surface 204 with less surface movement and less tendency to agglomerate together. The low reaction energy, the low surface mobility, and the low deposition rate of the reduction chemistry may provide increased uniformity and less agglomeration, which may lead to better adhesion of the conductive film layer during the nucleation process stage. Good adhesion during the initial stage of the conductive film formation process produces a semiconductor device film layer with less internal defects, which serves to improve the functionality, integrity, and reliability of the device. Also, residual hydrogen bonding of conductive elements to the semiconductor substrate surface may also contribute to the good nucleation adhesion.

Figure 2B graphically illustrates the results of further growth of the initial nucleation sites. After the nucleation process is complete, the first reactant vapor 126 is

no longer introduced into the CVD chamber 102. Instead, the second reactant vapor 128 is simultaneously introduced into the CVD chamber 102 along with the precursor gases 104a, 104b. The second reactant vapor 128, in one embodiment, serves as an oxidizing agent that reacts with the precursor gases 104a, 104b, and, due to its high reaction energy, the applied oxidation chemistry results in rapid columnar growths 208 above the initial nucleation sites that were deposited with reduction chemistry on the semiconductor substrate surface 204. The high reaction energy state may provide for an increased surface mobility as the metal-organic molecules begin to adhere to the semiconductor surface 204 which results in the metal atoms agglomerating together into the columns. The fast columnar growth tends to leave gaps 210 and pinholes 212 between the grain structures of the conductive elements. These flaws may be corrected with the application of another reduction chemistry process, which will be further described herein below. In one embodiment, the second reactant vapor 128 is comprised of an oxygen containing gas such as N_2O, O_2, NO or O_3.

Figure 2C graphically illustrates the subsequent processing- step of repeating the application of reduction chemistry to the semiconductor device 200. After the oxidation layer 208 is complete, the second reactant vapor 128 is no longer introduced into the CVD chamber 102, but, instead, the first reactant vapor 126 is introduced into the CVD chamber 102 along with the introduction of the precursor gases 104a, 104b. Due to the lower reaction energy and the resulting lower surface mobility of depositing conductive elements with reduction chemistry, inserting a conductive layer deposited with reduction chemistry interposed between two conductive layers deposited with oxidation chemistry may serve to disrupt the grain structure in the direction normal to the semiconductor surface 204. In addition, the slow depositions rates of reduction chemistry may tend to fill in the gaps and pinholes left by the rapid growth rates of oxidation chemistry.

Figure 2D graphically illustrates that the next layer of oxidation chemistry will grow more uniformly. As is illustrated in Figure 2D, the use of the oxidation chemistry

by the introduction of the second reactant vapor 128, results in quicker growth of the thin film layer, as discussed above. However, as is illustrated in Figure 2E, alternating reduction and oxidation chemistry processes results in an improved grain structure as a result of the reducing chemistry filling in more of the gaps and pin holes. The process of alternating reduction and oxidation chemistries may be repeated until the desired thickness of the conductive layer is achieved.

The advantage of utilizing reduction chemistry for the initial nucleation phase is the reduced surface mobility of the metallic molecules, such as platinum, rhodium, and/or a combination thereof. A reduced surface mobility of the metallic molecules results in a more uniform coverage of the semiconductor surface 204, improved adhesion and improved morphology of the metallic molecules onto the semiconductor surface 204. The uniform coverage is the result of less agglomeration of the metallic molecule during the reduction chemistry phase of the MOCVD process, which results in a reduction of gaps and pinholes in the conductive film layer. Additionally, there may also be some residual hydrogen bonding between the substrate molecules and the metallic molecules, which may also contribute to the improved adhesion of the metallic molecules onto the semiconductor substrate surface.

Furthermore, the advantage of utilizing oxidation chemistry after the reduction chemistry is that oxidation reactions involve higher reaction energies, which result in an increased surface mobility of the metallic molecules, such as platinum and rhodium. The higher reaction energy of the metallic molecules increases the agglomeration rate, which results in a rapid columnar growth rate. Although the rapid growth rate may cause poorer adhesion and morphology, such that gaps and pinholes in the film layer more readily occur, the addition of another reduction film layer interposed between two oxidation layers tends to reduce the problems of poorer adhesion morphology.

Another advantage to alternating the reduction and oxidation chemistries is that reduction contaminates, such as carbon, left behind by the metal-organic reduction reactions may be burned out of the conductive film layer during the oxidation process,

which improves the overall purity and cohesion of the metallic molecules to each other and to the semiconductor surface. Additionally, the process of alternating the reduction and oxidation chemistries produces metal-organic deposition layers that exhibit the ability to maintain a uniform topography, wherein the deposited layers have a substantially flat and smooth surface. The improved morphology results in the reduction of surface defects, such as step layer thinning, cracks, and surface reflections.

In one particular example of the above process, a conductive layer 220 is formed using an initial deposition step, wherein a platinum-rhodium precursor carrier gas is provided from the conductive carrier gas source 116 through the bubbler 114 at a rate of between 5 to 300 sccm with the platinum-rhodium being encapsulated within a helium carrier. The bubbler 114 contains a liquid precursor at a temperature between 20°C and 200°C, such that the resulting precursor gases 104a, 104b emanating from the bubbler 114 has the chemical composition as illustrated in Figure 3A and 3B. The resulting precursor gases 104a, 104b is provided from the bubbler 114 to the CVD chamber 102 along with an initial simultaneous introduction of H_2 reactant 126 at a rate of 50 to 1000 sccm from the reactant source 122. This introduction of precursor gases 104a, 104b and reactant 126 is provided to the CVD chamber 102 for approximately 50 seconds to result in deposition of the nucleation sites 206. At the end of the approximately 50 second nucleation period, the introduction of the precursor gases 104a, 104b from the bubbler 114 is continued while the introduction of the N_2O reactant 128 from the reactant source 124 is continued for approximately 50 seconds. The N_2O thus comprises the reactant 128, which reacts with the metal-organic compounds comprised by the precursor gases 104a, 104b in the deposited layer 160 to further grow the conductive layer 220. These two process steps are alternately repeated until a conductive layer or element of a desired thickness is formed.

From the foregoing, it will be appreciated that the above-described metal-organic chemical vapor deposition process illustrates a method of forming a conductive film layer 220 or structure on a semiconductor device 202 that results in a more uniform

conductive film structure with improved adhesion and morphology. This results in a significantly efficient conductive device that exhibits improved conduction and less resistivity between grain interfaces. Moreover, the improved efficiencies may also result in faster devices that exhibit improved reliability and functionality overall.

Although the foregoing description of the preferred embodiment of the present invention has shown, described and pointed out the fundamental novel features of the invention, it will be understood that various omissions, substitutions and changes in the form of the detail of the apparatus as illustrated as well as the uses thereof, may be made by those skilled in the art without departing from the spirit of the present invention. Consequently, the scope of the present invention should not be limited to the foregoing discussions, but should be defined by the appended claims.